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THERMAL DECOMPOSITION OF $[Co(NH_3)_5Cl]Cl_2$
I. Non-isothermal, quasi-isothermal and scanning electron microscopy studies

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Simultaneous TG-DTG-DTA studies on $[Co(NH_3)_5Cl]Cl_2$ under non-isothermal conditions were carried out in dynamic air and argon atmospheres in the temperature range 293-1273 K. Thermogravimetric measurements under quasi-isothermal conditions were also made. On the basis of the experimental data (weight loss, X-ray diffraction, reflectance spectroscopy and chemical analysis), the probable decomposition sequences are presented. The data indicate that the thermal decomposition of $[Co(NH_3)_5Cl]Cl_2$ occurs in three stages in argon and four stages in air.

The changes in the morphology of crystalline $[Co(NH_3)_5Cl]Cl_2$ powder in the course of its thermal decomposition in air were followed by scanning electron microscopy.

The literature data relating to the thermal decomposition of $[Co(NH_3)_5Cl]Cl_2$ are just as numerous as for $[Co(NH_3)_6]Cl_3$. The early work published on this subject was reviewed by Wendlandt and Smith [1]. The TG-DTA curves and dissociation sequences of this compound have been presented by many investigators [1-7]. Generally, it may be said that the thermal decomposition sequences suggested for $[Co(NH_3)_5Cl]Cl_2$ are the same as for compounds of the type $[Co(NH_3)_6]X_3$ (X = Cl, Br).

Wendlandt concluded [1, 2, 6, 7] that the intermediates of dissociation of the title compound in a helium atmosphere are $(NH_4)_2[CoCl_4]$ and $CoCl_2$. Additionally, *trans*-$[Co(NH_3)_4Cl_2]Cl$ was identified in vacuum.

There are no published data regarding morphological studies of the intermediates of $[Co(NH_3)_5Cl]Cl_2$ dissociation. It is considered that a combination of the results of morphological and kinetic investigations and other experimental methods might shed light on the macromechanism of the particular stages of thermal decomposition of $[Co(NH_3)_5Cl]Cl_2$.

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This amminecobalt complex seems to be interesting as an intermediate in cobalt recovery technology [8].

In the present work, the thermal decomposition of $[Co(NH_3)_5Cl]Cl_2$ has been studied in air and argon atmospheres under non-isothermal and quasi-isothermal conditions. The changes in the morphology of the crystalline $[Co(NH_3)_5Cl]Cl_2$ powder were followed in the course of thermal decomposition in air.

Experimental

Materials

All reagents were of AnalaR grade. Pentaamminecobalt(III)chloride was prepared by the method described in [9]. The starting compound was characterized via the methods of elemental analysis. The results of the analysis were: Co, 24.0% found, 23.5% calc.; H, 6.4% found, 6.1% calc.; N, 27.7% found, 27.9% calc.; Cl, 41.9% found, 42.5% calc.

A particle size of ≤ 0.060 mm with a specific surface of 5.21 m^2g^{-1} was used.

Methods

The thermal analysis, X-ray diffraction, reflectance spectroscopy and morphological measurements were made as reported in the previous paper [10] of the present series.

Results and discussion

TG and DTA curves similar to those reported previously [1-5] were obtained. The thermoanalytical data show that the thermal decomposition of $[Co(NH_3)_5Cl]Cl_2$ proceeds in three stages in argon atmosphere, and in four stages in air, like the dissociation of $[Co(NH_3)_6]Cl_3$ [10]. The temperature ranges and percentage weight losses of the particular decomposition stages, together with the other thermoanalytical data, are given in Table 1.

All the decomposition reactions are endothermic in both air and argon atmospheres. For the first and second stages of the investigated dissociation, the percentage weight losses are the same in the two gaseous atmospheres (see Table 1). The temperatures of the DTA and DTG peaks and also the temperature ranges for stages I and II are slightly higher in argon than in air. It may be assumed that the transformations occurring are independent

Table 1 Thermoanalytical results (TG-DTG-DTA) on $[Co(NH_3)_5Cl]Cl_2$ decomposition in air and argon atmospheres. Heating rate 1.25 deg/min

Stage	Temp., range K	DTG_{max}, K	DTA peak temp., K	Weight loss, %		Composition of residue	Atmosphere
				Observ.	Theor.		
I	433-543	538	538	27.0	26.7	$CoCl_2 + (NH_4)_2CoCl_4$	air
	488-543	541	541	27.0	26.7	$CoCl_2 + (NH_4)_2CoCl_4$	argon
II	543-623	618	618	23.0	21.4	$CoCl_2$	air
	543-618	613	618	22.0	21.4	$CoCl_2$	argon
III	623-873	858	858	20.5	19.8	Co_3O_4	air
	618-1143	1043	998	23.5	Sublimation	$CoCl_2$	argon
IV	1203-1218	1208	1208	2.5	2.2	CoO	air

Table 2 Quasi-isothermal analysis data (Q-TG) on $[Co(NH_3)_5Cl]Cl_2$ decomposition in air and nitrogen atmospheres. Heating rate 3 deg/min; rate of transformation 0.4 mg/min

Stage	Temp., range	Weight loss, %		Composition of	Atmosphere
	K	Observ.	Theor.	residue	
I	443-518	27.2	26.7	$CoCl_2 + (NH_4)_2CoCl_4$	air
	473-525	26.4	26.7	$CoCl_2 + (NH_4)_2CoCl_4$	nitrogen
II	518-598	21.6	21.4	$CoCl_2$	air
	525-605	22.4	21.4	$CoCl_2$	nitrogen
III	598-938	18.8	19.8	Co_3O_4	air
	605-1078	30.4	subl.	$CoCl_2 + Co_{met} + CoO$	nitrogen

of the gaseous atmosphere. However, for the third stage the observed temperature parameters and weight losses are clearly different in air and argon. The fourth stage of the dissociation of $[Co(NH_3)_5Cl]Cl_2$ was observed in air atmosphere only, just as for $[Co(NH_3)_6]Cl_3$ [10].

These data are generally consistent with those published earlier [1-3, 5]. The temperatures of the DTA peaks (stages I and II) are mostly close to those reported by Watt (554 and 613 K - N_2 atm.) [3] and to the values determined for the thermal decomposition of $[Co(NH_3)_6]Cl_3$ (535 and 623 K - air atm., and 533 and 623 K - Ar atm.) [10].

The thermogravimetric results obtained for $[Co(NH_3)_5Cl]Cl_2$ decomposition under quasi-isothermal conditions (Table 2) in air and nitrogen atmospheres confirm the non-isothermal data.

The inflection points and the weight losses observed in TG and Q-TG measurements during the first and second stages are in accordance with the sequences of $[Co(NH_3)_5Cl]Cl_2$ dissociation reported by Wendlandt and Smith [1, 2].

It is commonly known that all reactions of thermal decomposition of ammine- and amminecobalt(III) complexes involve the reduction of Co(III) to Co(II) [1-3, 7, 10, 11].

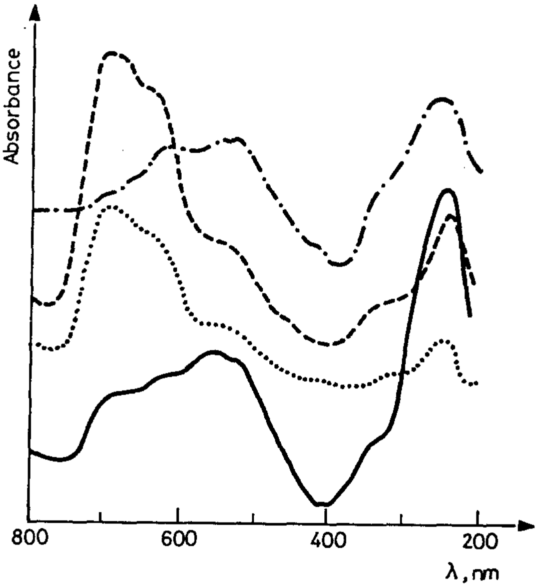

Fig. 1 Reflectance spectra of some cobalt(II) compounds. — decomposition products of $[Co(NH_3)_5Cl]Cl_2$ at 558 K, ······ $(NH_4)_2[CoCl_4]$, ---- 1:1 mixture of $CoCl_2+(NH_4)_2[CoCl_4]$, -·-·- $CoCl_2+NH_4Cl$ mechanically mixed mixture

The probable decomposition sequence for $[Co(NH_3)_5Cl]Cl_2$ is:
stage I (air, argon):

$$6\,[Co(NH_3)_5Cl]Cl_2 \rightarrow 3\,CoCl_2 + 3\,(NH_4)_2[CoCl_4] + N_{2(g)} + 22\,NH_{3(g)} \quad (1)$$

stage II (air, argon):

$$3\,(NH_4)_2[CoCl_4] \rightarrow 3\,CoCl_2 + 6\,NH_4Cl_{(g)} \quad (2)$$

The presence of $(NH_4)_2[CoCl_4]$ as a component of the solid intermediate near the end of the first dissociation stage was confirmed by spectroscopic measurements, just as for $[Co(NH_3)_6]Cl_3$ decomposition [10, 12]. In the course of heating of $[Co(NH_3)_5Cl]Cl_2$ under quasi-isothermal conditions at 558 K (weight loss = 28%), i.e. at the beginning of the second stage of decomposition, a deep-blue species was isolated, similarly as described in [10]. The reflectance spectrum of this species is shown in Fig. 1.

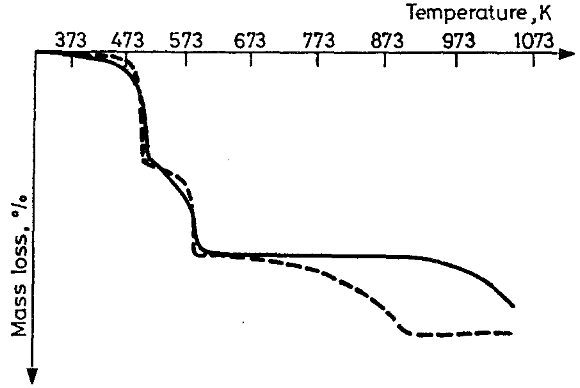

Fig. 2 Q-TG curves of $[Co(NH_3)_5Cl]Cl_2$ — in nitrogen, --- in air

For comparison, the reflectance spectra of $(NH_4)_2[CoCl_4]$ a 1:1 mixture of $CoCl_2$-$(NH_4)_2[CoCl_4]$ (prepared as in [12]) and a mechanically mixed 1:1 mixture of $CoCl_2$-NH_4Cl are also presented. The reflectance spectrum of the isolated intermediate resembles most the spectrum of the last-mentioned mixture. However, the clear shoulders observed at 690 and 670 nm, as well as the absorption band at 234 nm, indicate the presence of the tetrahedral ion $[CoCl_4]^{2-}$ (transitions $^4T_1(P) \rightarrow {}^4A_2$ and charge transfer, respectively) [13].

The shoulder at about 585 nm can originate from $CoCl_2$ ($^4T_{1g}(P) \rightarrow {}^4T_{1g}$ transition) [13]. It suggests that the reflectance spectrum of the isolated intermediate (beginning of stage II) in Fig. 1 should be the spectrum of the mixture of $CoCl_2$, $(NH_4)_2[CoCl_4]$ and NH_4Cl, which is in agreement with the thermal decomposition sequence (1,2) assumed. The presence of $(NH_4)_2CoX_4$ as a solid intermediate in the decomposition of cobalt(III)ammine complexes has been confirmed by several investigators [1-3, 7, 10, 12, 14].

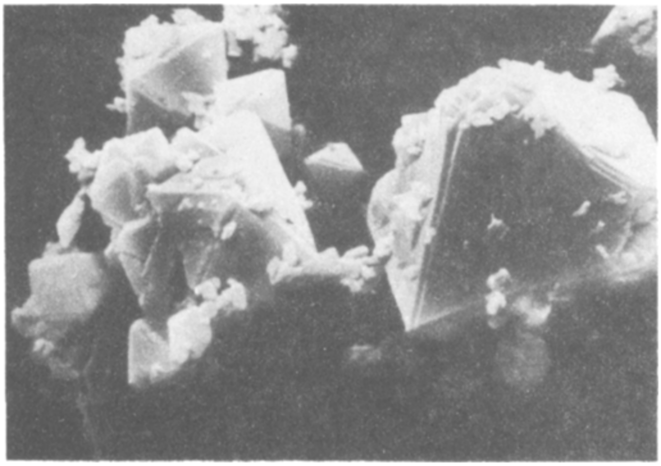

Fig. 3 Scanning electron micrograph of crystalline $[Co(NH_3)_5Cl]Cl_2$ powder (magnification 3000x)

In the third stage of $[Co(NH_3)_5Cl]Cl_2$ dissociation in air, the reaction of cobalt(II) chloride with oxygen is followed by the evolution of chlorine, and Co_3O_4 is formed as a stable solid residue, as in $[Co(NH_3)_6]Cl_3$ decomposition [10], which was confirmed by X-ray diffraction analysis. The evolution of chlorine was confirmed by a standard method, as described earlier [10].

In the fourth stage, Co_3O_4 is transformed to CoO, which is in agreement with the literature data [10, 14, 15].

The reactions in stages III and IV in air were found to be:

$$3\,CoCl_2 + 2\,O_{2(g)} \rightarrow Co_3O_4 + 3\,Cl_{2(g)} \tag{3}$$

$$Co_3O_4 \rightarrow 3\,CoO + 1/2\,O_{2(g)} \tag{4}$$

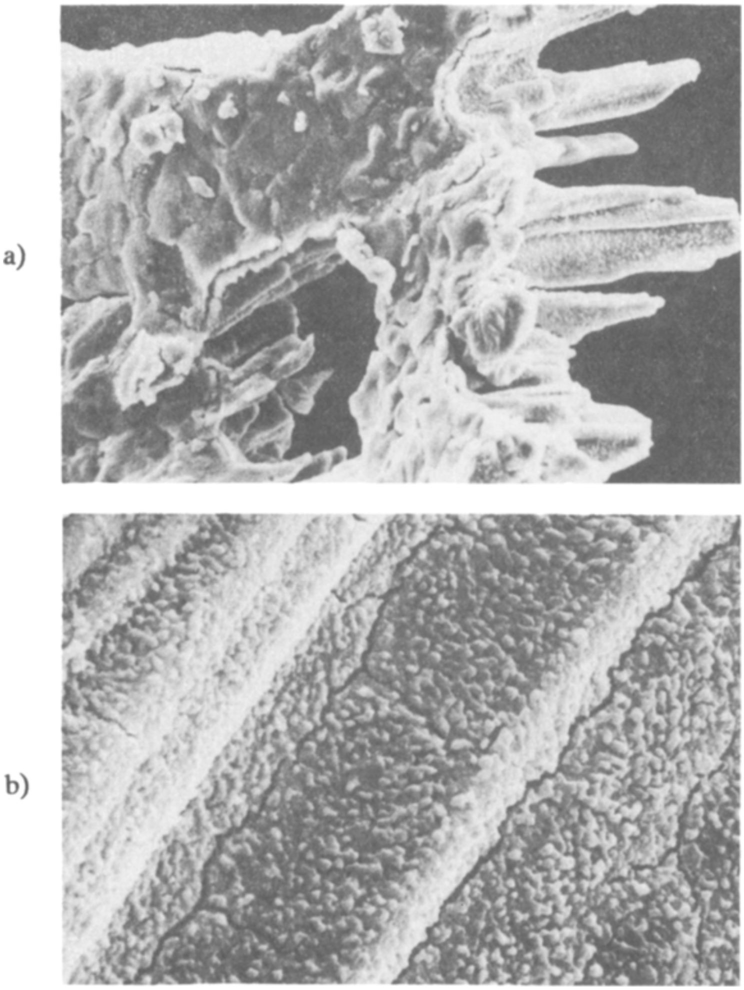

Fig. 4 Scanning electron micrographs of intermediate A – final residue of first stage of $[Co(NH_3)_5Cl]Cl_2$ decomposition in air. a) magnification 1000x, b) magnification 3000x

The third stage of $[Co(NH_3)_5Cl]Cl_2$ dissociation in flowing argon atmosphere runs like that for $[Co(NH_3)_6]Cl_3$ decomposition [10]. In the course of this stage, $CoCl_2$ appears to sublime:

$$CoCl_{2(s)} \rightarrow CoCl_{2(g)} \qquad (5)$$

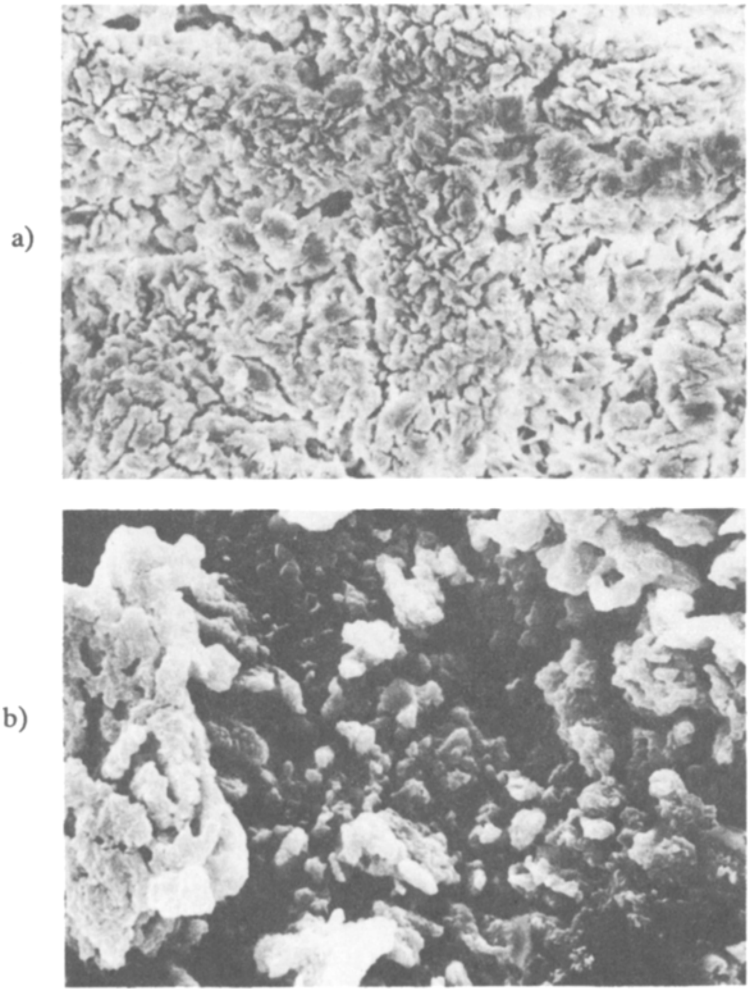

Fig. 5 Scanning electron micrographs of intermediate B – final residue of second stage of $[Co(NH_3)_5Cl]Cl_2$ decomposition in air. a) magnification 1000x, b) magnification 3000x

Some reduction of $CoCl_2$ probably occurs as a result of the secondary reaction of $CoCl_2$ with NH_3 (6). On the blue-coloured walls of the crucible, single grains of cobalt metal were observed:

$$3\,CoCl_2 + 2\,NH_{3(g)} = 3\,Co + N_{2(g)} + 6\,HCl_{(g)} \qquad (6)$$

$$(\Delta G^{0}_{800\,K} = -60.92\,kJ\ [10])$$

The presence of some cobalt metal was revealed by X-ray analysis in the final solid residue of $[Co(NH_3)_5Cl]Cl_2$ decomposition under quasi-isothermal conditions in nitrogen atmosphere, just as observed for $[Co(NH_3)_6]Cl_3$ dissociation [10].

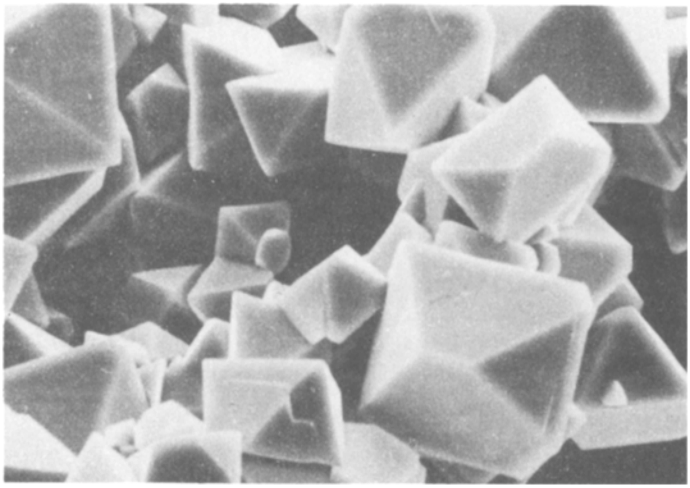

Fig. 6 Scanning electron micrograph of intermediate C – final residue of third stage of $[Co(NH_3)_5Cl]Cl_2$ decomposition in air (magnification 3000x)

The sublimation of $CoCl_2$ and the formation of cobalt metal as a result of the decomposition of $[Co(NH_3)_5Cl]Cl_2$ in vacuum was also observed by Wendlandt and Collins [7].

The changes in the morphology of crystalline $[Co(NH_3)_5Cl]Cl_2$ powder in the course of its thermal decomposition in air at 298-973 K were observed by using scanning microscopy in the manner described in [10]. On the basis of the Q-TG curve (Fig. 2), the solid intermediates which were the final residues after the particular stages of substrate decomposition (stages I-III) were isolated from the system investigated. Samples of the pentaamminecomplex were heated under quasi-isothermal conditions up to the temperatures listed in Table 3.

The process was then interrupted and, after quenching, intermediates were prepared for microscopic measurements.

The scanning electron micrographs of the substrate and investigated intermediates are presented in Figs 3-6. The results showed that, even in the first stage of the thermal decomposition (intermediate A), a clear change occurred in the substrate morphology.

Table 3 Samples for scanning electron microscopy analysis

Stage	Weight loss, %	Temp., K	Colour	Intermediate
I	28.0	558	deep-blue	A
II	48.8	598	blue	B
III	68.0	973	black	C

The surface of the polycrystalline powder diminished and the structure became more compact, probably as a result of the sintering process with the share of a liquid phase (rounded edges of the grains). Numerous visible pores and cracks (a spongy macrostructure) were probably caused by the intensive evolution of the gaseous products of decomposition, i.e. NH_3 and N_2. It may be noted (Fig. 4) that intermediate A consists of two compounds, probably $CoCl_2$ and $(NH_4)_2[CoCl_4]$ as mentioned above (see Eq. 1).

In the course of stage I, the pseudooctahedral structure of $[Co(NH_3)_5Cl]^{2+}$ is converted into the structures of the intermediates, i.e. octahedral $CoCl_2$ and tetrahedral $(NH_4)_2[CoCl_4]$. Simultaneously, reduction of the central Co(III) to Co(II) and the liberation of NH_3 and N_2 occurred. All this probably caused local stress in the crystallites and their cracking, which was observed (Fig. 4) in the micrographs.

Intermediate B, the final product in the second stage of $[Co(NH_3)_5Cl]Cl_2$ decomposition, appears to have a clearly more cracked and porous structure (Fig. 5) than intermediate A. The pores are considerably larger, and a substantial proportion of them involve cavities, which is probably connected with NH_4Cl sublimation (see Eq. 2).

Intermediate C, the end-product of the third stage of decomposition of $[Co(NH_3)_5Cl]Cl_2$ (Co_3O_4 as confirmed by the X-ray pattern) has a distinctly crystalline structure (Fig. 6). There are octahedra of different sizes, this being one of the regular system shapes [16]. The micrograph (Fig. 6) illustrates nucleation and liberation of the nucleus from the face of the crystals. The crystals of Co_3O_4 (Fig. 6) obtained as the final product of thermal decomposition of $[Co(NH_3)_5Cl]Cl_2$ have the typical form of crystals originating from melts. It should be noted that this Co_3O_4 has just the same crystalline form as Co_3O_4 obtained from $[Co(NH_3)_6]Cl_3$ decomposition [10].

Conclusion

The thermal decomposition of $[Co(NH_3)_5Cl]Cl_2$ occurs in three and four stages in argon and air atmospheres, respectively, just as observed for $[Co(NH_3)_6]Cl_3$ dissociation [10]. The courses of the first and second stages of decomposition are the same in the two atmospheres, but the third stage differs in air and argon. The sequences determined are in agreement with those proposed by Wendlandt *et al.* [1, 2].

The final products (Co_3O_4) of the thermal dissociations of $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_6]Cl_3$ [10] have the same crystalline form.

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Zusammenfassung — In dynamischer Luft- und Argonatmosphäre wurden im Temperaturbereich 293-1273 K unter nichtisothermen Bedingungen simultane TG-DTG-DTA Untersuchungen an $[Co(NH_3)_5Cl]Cl_2$ durchgeführt, ebenso auch thermogravimetrische Untersuchungen unter quasi-isothermen Bedingungen. Auf der Grundlage der experimentellen Daten (Gewichtsverlust, Röntgendiffraktion, Reflexionsspektroskopie und chemische Analyse) wurde eine wahrscheinliche Zersetzungssequenz erstellt. Es zeigte sich, daß die thermische Zersetzung in Argon in drei Schritten, in Luft dagegen in vier Schritten verläuft

Die Veränderung der Morphologie kristallinen $[Co(NH_3)_5Cl]Cl_2$-Pulvers im Verlaufe seiner thermischen Zersetzung in Luft wurde durch Scanning-Elektronenmikroskopie verfolgt.